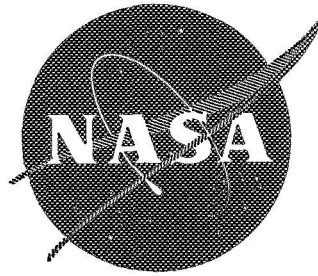# EVAPORATION RATE OF MERCURY AS AFFECTED BY SMALL PROPORTIONS OF CONTAMINANTS

by

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prepared for

National Aeronautics and Space Administration

April 20, 1970

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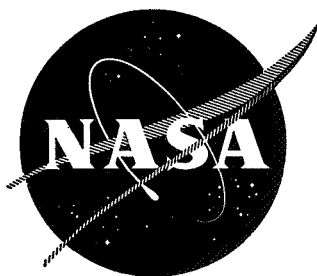
Final Report

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ABSTRACT

The evaporation rate of pure mercury was compared to that of mercury dosed to the extent of .02% (200 ppm) with eleven different metallic contaminants. The evaporations were performed at 5×10^{-6} Torr and 24°C. Four of the contaminants, magnesium, sodium, lithium and tin, lowered the evaporation rate to less than 1% that of the pure mercury. The molecular mechanism of the lowering was not established.

SUMMARY

The evaporation rates of pure mercury and mercury dosed with 200 ppm (.02%) of eleven different metallic contaminants were compared. The contaminants were Na, Mg, Zn, Ga, Cd, In, Sn, Pb, Ag, Bi, and Li. The evaporations were performed at 5×10^{-6} Torr and 24°C. All the contaminants decreased the evaporation rate significantly. The least effective contaminant (silver) decreased it to 52% that of pure mercury; the most effective (tin, magnesium, sodium and lithium) to less than 1% that of pure mercury. The possibility of oxide film formation existed since the prevailing pressure did not preclude it, and since all the contaminants have a higher electrode potential than mercury. Of the four highly inhibiting contaminants sodium is the only one which could possibly be acting in elemental form via a Gibbsian-adsorption mechanism. The remaining three could possibly be acting via Gibbsian adsorption if we postulate either intermetallic compound formation with the mercury (or association in solution) or a soluble oxide formation. All four could possibly be acting via formation of a simple surface oxide film. This latter mechanism would presumably be unsatisfactory under space conditions, because there would be insufficient oxygen present to heal the film if ruptured. A Gibbsian adsorption mechanism is considered necessary for satisfactory performance in space.

Evaporation Rate of Mercury as Affected by
Small Proportions of Contaminants

Introduction

Although mercury is a desirable material for certain components of
space vehicles it suffers from the disadvantage of having a relatively high
evaporation rate under the prevailing hard vacuum conditions in space. It
is known that non-volatile surface films as thin as a single molecule are
in some cases capable of significantly retarding the evaporation rate of
liquids. It is also known from recent work[1] that very small proportions
of soluble metallic impurities cause films to form on the surface of mercury
under ordinary atmospheric conditions, and that these films have an
unexpectedly high content of the contaminant metal. It was considered
possible that films of this type might be formed under space conditions,
that they might be self-healing or self-renewable when mechanically disrupted,
and that they might lower the evaporation rate of mercury sufficiently to
make it useful. It was considered imperative for engineering purposes that
the percentage of contaminant be sufficiently low to have no significant
effect on the bulk properties of the mercury, and therefore a maximum con-
taminant concentration of 200 parts per million (.02%) was arbitrarily set.
The object of this investigation was to compare the evaporation rates of
pure mercury and mercury contaminated with 200 ppm of 10 different soluble
metals at a fixed temperature ($24°\pm5°C$) and a measured pressure less than
10^{-5} Torr.

Experimental

The mercury samples while being evaporated were contained in small
diameter glass tubes supported vertically and initially filled to the brim.
The apparatus was designed to introduce the pre-cut and weighed contami-
nant metals into the pre-weighed mercury, which was held in shallow troughs,
allow the contaminants to dissolve, load the tubes, tilt them back to the

upright position, and dispose of the residual mercury in the troughs by pouring it into a cold trap at the bottom of the apparatus; all under high vacuum except for the tube loading which was done under dry helium. Three samples were handled simultaneously, one of them always being pure mercury and each of the other two a different contaminated sample. The three tubes were placed close together, and the rate of evaporation was monitored by measuring the progressive decrease in level of the mercury by means of a cathetometer. Thus in a single run, which generally proceeded for at least two or three days, the evaporation rates of two contaminated samples could be compared with that of pure mercury. The measurements were always comparative, and the evaporation rates of the contaminated samples are expressed in the Results section as percentages of the evaporation rate of pure mercury. This is because the absolute evaporation rates varied widely from run to run. This was not surprising, since the rates depend greatly on the location of the solid mercury condensate in the cold finger of the bell jar surrounding the evaporation unit (see Appendix, page A-2). In normal operation mercury vapor condenses on the inner wall of this cold finger just at or slightly below the level of the liquid nitrogen bath outside. As the nitrogen evaporates and its level becomes lower the upper portions of condensed mercury can become warm and evaporate in competition with the test sample. Since the nitrogen was replenished by a timer which periodically injected a fixed quantity, rather than on the basis of liquid level, the amount of evaporation from this source within any given time period was far from constant. Details of the apparatus and the experimental procedure are given in the Appendix.

The eleven metals used as contaminants,aand their properties, are listed in Table 1. These metals were chosen for the following reasons: 1. They are available and procurable in highly pure form. 2. They are sufficiently soluble in mercury. 3. They represent a range of reactivity, i.e. susceptibility to oxidation. 4. They represent a range of surface tensio. bracketing that of mercury. The last column of Table 1 lists surface tensions of some of the 200 ppm contaminated mercury samples, as measured in this laboratory by the bubble pressure method (details in the

Appendix). Two of the metals, Li and Na, were introduced as concentrated amalgams which had been prepared in air immediately beforehand. All others were introduced in vacuum as pure metal.

Results

Of the nine metals which were introduced into the mercury under high vacuum only two, tin and silver, caused no diminution in the visual brightness of the mercury surface. Lead, zinc, bismuth and cadmium showed some dulling, presumably due to a thin oxide film. Gallium and indium, and especially magnesium, showed appreciable dulling. The lithium and sodium amalgams showed somewhat less dulling. Magnesium formed a film of definitely frosty appearance. The magnesium, sodium, gallium and lithium samples showed a strong tendency to wet the glass capillaries, and even the Teflon trough, when they first contacted them under vacuum. Later, when the vacuum was released they balled up on both surfaces in normal fashion. This could be an effect of atmospheric moisture or possibly of electrostatic charging, but we have no evidence as to the real cause, nor was any attempt made to discover it.

Evaporation rates are shown in Table 2. The metals appear to fall into three groups: Lead and silver allowed considerable evaporation, although even these contaminants reduced the evaporation rate to a remarkable extent considering their extremely low concentration. Tin, magnesium, sodium and lithium reduced the evaporation rate to less than 1% that of pure mercury. The other five metals had an intermediate effect.

Discussion

The theory of the effect of thin surface films on the evaporation rate of liquids is relatively well worked out[2,3]. The surface film acts as one of the important energy barriers which the escaping molecule must overcome on its path from the interior of the liquid to the remote region of the vapor phase. The extent to which it acts as a barrier depends on its chemical constitution, its thickness, and its physical state, and our data can be discussed in terms of these three properties.

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If we take a binary solution consisting of 99.98% mercury and .02% of another metal (the "contaminant") that does not form an intermetallic compound with the mercury, the composition of the liquid-vapor interface can be calculated by thermodynamics. Assuming that the vapor phase contains no molecular species other than those in the liquid, the quantitative relationship is given by the Gibbs absorption equation, a simplified form of which for dilute binary solution is:

$$\Gamma_2 = -\frac{C_2}{RT}\frac{\partial \gamma}{\partial C_2}$$

where Γ_2 is the surface excess of solute, C_2 is the concentration of solute, γ is the surface tension of the solution and R and T have their usual significance. If this equation is used for computation the concentration units and energy units should be consistent. Γ_2 and C_2 for example, can be in moles per liter, γ in dynes/cm, R in ergs per °C, and T in degrees Kelvin. Coupled with the fact that the surface tension of a binary liquid mixture lies between that of the two components and is single valued (at constant temperature) this equation tells that the component of lower surface tension becomes concentrated in the surface. The surface tensions of both components must be valued at the temperature of the experiment, which is, of course, impossible for solid solutes. It is an invariable rule, however, that the surface tension of a pure substance increases monotonically with decreasing temperature. Referring to Table 1 it is evident that only gallium and sodium can reliably be expected to have a surface tension lower than that of mercury in the mixture at 24°C. The surface tension of lithium, bismuth and lead, extrapolated back to this temperature, would be higher than that of mercury; and the surface tensions of the remaining metals are already higher than that of mercury, even at their high melting points. Sodium and gallium, therefore, are the only metals of the group tested which could become concentrated in the surface in an inert atmosphere. The remaining metals would be negatively surface active, i.e. the surface concentration would be less than the bulk concentration. It is difficult to conceive how the surface tension lowerings that were observed could be due to these pure metal contaminants.

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The electrochemical potential data in Table 1 show that all the metals tested, even silver, are more electropositive than mercury and will therefore tend to oxidize in the presence of mercury. This fact is also borne out in the case of certain metals by previous work[1]. The dull coated appearance of all the contaminated samples, with the notable exceptions of tin and silver, also suggests that an oxide film was formed even at the low pressure used. The surface tension measurements that were made on mercury and on five of the contaminated mercury samples offer little further help in arriving at a valid explanation of the startling effect on evaporation rate. Silver has no measurable effect on the surface tension. This is the expected behavior. Zinc, which lowers the evaporation rate greatly and dulls the surface slightly, has no significant effect. The range noted is due to experimental difficulties. The effect of gallium is real though slight and is expected on the basis of the surface tension of gallium. Sodium has a very pronounced effect, which checks the literature value quite well[4] and which is expected from the low surface tension of sodium. Tin, which forms no visible film, lowers the surface tension significantly, at least 60 dynes/cm. This could be due to formation of a tin-mercury intermetallic compound (hypothesized) which would have to have a lower surface tension than mercury. It cannot be due, on thermodynamic grounds, to tin alone unless the tin exists in some unknown associated form in the liquid mercury.

The evaporation-inhibiting effect of zinc and the much less pronounced effect of silver we are inclined to attribute to oxide formation. The silver oxide may simply be invisible, i.e. have an optical character such that it does not diminish the luster of the pure mercury. Or the silver oxide may be truly soluble in the mercury and form the inhibiting film by surface activity according to the Gibbs equation. We may hypothesize an exactly similar picture for tin, and assume that the tin oxide is a more effective evaporation barrier than silver oxide. Sodium might also have exerted the observed evaporation-inhibiting effect via an oxide, even though it is theoretically capable of so acting in its elemental state. In support of this view is the visible change of the mercury surface caused by sodium.

It is of considerable importance to know the mechanism of the inhibition. If it is due to an insoluble oxide film, as appears probable but not certain for magnesium and lithium, these substances would probably not be functional in the space environment. The oxide film could not form because of the extremely low oxygen pressure, and even if performed at low altitude it could not repair itself if ruptured. If it is due to pure metal (a possibility with sodium) or to a mercury-soluble intermetallic compound (a possibility with tin) or to a mercury-soluble oxide (a possibility with all four metals of interest, but especially with tin because its luster is undimmed) then the substances would be functional. The film would form and repair itself in the complete absence of oxygen. If soluble oxide is the active agent it would be used instead of the elemental metal as a contaminant.

Conclusions

All contaminants tested inhibited the evaporation significantly, and four of them (sodium, lithium, magnesium and tin) reduced it to a satisfactory level (less than 1% of pure mercury). Four mechanisms could possibly cause the effects noted:

(1) Formation of a Gibbsian-adsorbed elemental metal.

(2) Formation of an insoluble oxide film on the surface.

(3) Formation of a soluble Gibbsian-adsorbed intermetallic compound or association complex.

(4) Formation of a Gibbsian-adsorbed mercury-soluble oxide.

Since the systems would be used in the hard vacuum of space, mechanisms #1, #3 and #4 would indicate a satisfactory material, since the surface film would be rapidly self-repairing in the complete absence of oxygen. Mechanism #2 would be unsatisfactory since oxygen would be needed to repair a ruptured surface film.

Of the four satisfactory contaminants only sodium could be acting in the form of a Gibbsian-adsorbed elemental metal. The remaining three could conceivably be acting in the form of a soluble Gibbsian-adsorbed intermetallic compound or association complex, or a mercury soluble oxide. It is also possible that all four could be acting by the formation of a simple oxide film.

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Table 1

Properties of Metals Used

Metal	Surface Tension (dynes/cm) $\alpha^{t(°C)}$	Std. Electrode Potential[8] E° (volts)	Melting Point (°C)[9]	Measured Surface Tension at 24°C 200 ppm in Mercury
Li	$398^{186°(10)}$	3.045	186	---
Na	$222^{100°(5)}$	2.714	97.5	272
Mg	$563^{651°(10)}$	2.37	651	---
Zn	$753\pm10^{477°(5)}$	0.763	419.5	472-490
Ga	$358^{40°(5)}$	0.52	29.78	429-461
Cd	$630^{320°(5)}$	0.403	320.9	---
In	$543.8^{300°(6)}$	0.34	156.4	---
Sn	$526^{253°(5)}$	0.136	232	404-420
Pb	$453^{350°(5)}$	-0.126	327.4	---
Ag	$800^{970°(5)}$	-0.799	960.8	482
Bi	$388^{300°(5)}$	-----	271	---
Hg	$484.2^{25°(7)}$	-0.854	-38.7	482-486

Table 2

Comparative Evaporation Rate of Pure versus Contaminated Mercury.
Contaminant Present at .02% (200 ppm). Manifold Pressure = 5 x 10^{-6} Torr.

Run #	Contaminant	Total Evaporation time (hrs)	Length of column evaporated (cm)	Rate of evaporation as percentage of rate for pure mercury
1[a]	None	139	.127	100
1	Zinc	139	.005	4.2
1	Lead	139	.037	29.0
2[a]	None	88	.120	100
2	Bismuth	88	.013	10.8
2	Cadmium	88	.009	7.2
4	None	69	.153	100
4	Gallium	69	.019	12
4	Silver	69	.080	52
6	None	64	.130	100
6	Tin	64	0-.004[b]	0-3
6	Magnesium	64	0-.004	0-3
6a	None	231	.40	100
6a	Tin	231	0-.004	less than 1
6a	Magnesium	231	0-.004	less than 1
7	None	44	.20	100
7	Indium	44	.011	5.5
7	Sodium	44	0-.004	less than 2
8	None	145	.50	100
8	Sodium	145	0-.004	less than .8
8	Lithium	145	0-.004	less than .8

a. Runs 1 and 2 were made in capillary tubes of .025 cm diameter.
   The remaining runs were made in tubes of .065 cm diameter.
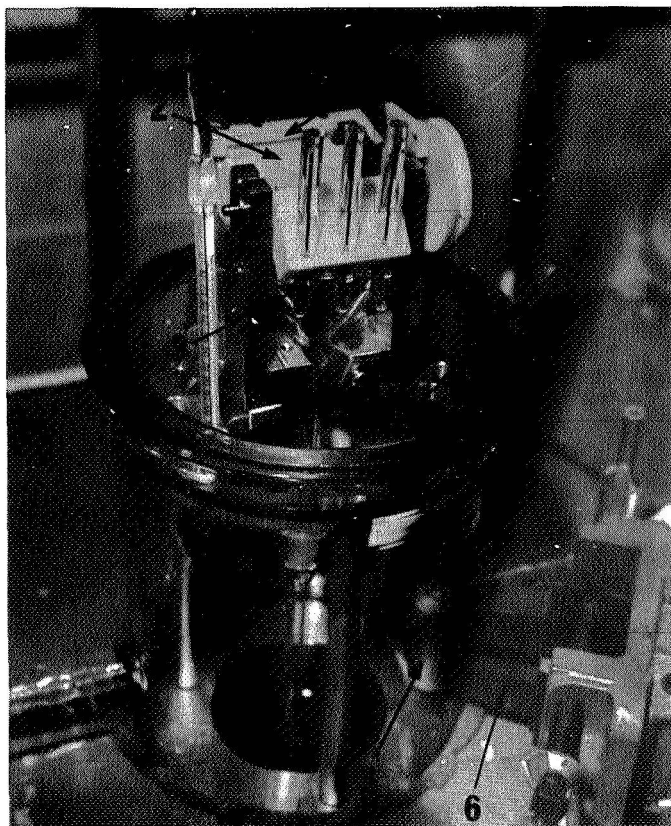
b. Standard deviation for 5 readings = ± .002 cm.

Figure 1

Vacuum System for Rate of Evaporation Experiments
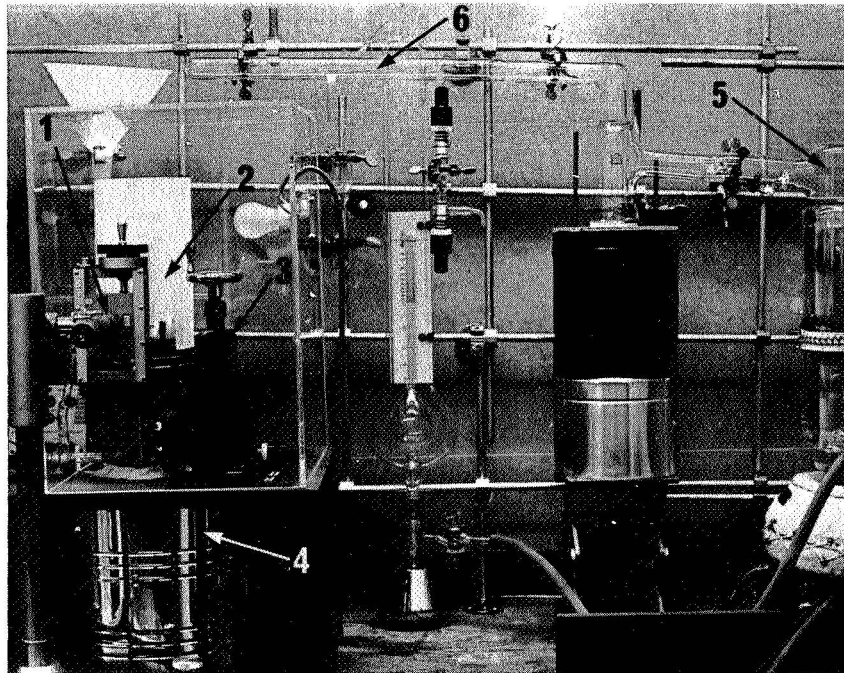
(1) Cathetometer

(2) Evaporation unit

(3) Vertical manipulator for outside magnet

(4) Stainless steel dewar

(5) Pump

(6) Manifold

Figure 2

Basic Elements of the Evaporation Unit

(1) Contaminant platform
(2) Mercury trough
(3) Rectangular funnel
(4) Brass counterweight
(5) Magnet counterweight
(6) Magnet

APPENDIX

I. Materials and Apparatus

All the contaminants in this study were obtained commercially and were used without further purification. Lead (#8 shot), cadmium (stick), zinc (stick), tin (bar), magnesium (ribbon), silver (wire), and lithium (metal lump) were obtained from Fisher Scientific Company; bismuth (99.999+%) and indium (99.999+%) sticks, from American Smelting and Refining Company; gallium (99.999%) metal lump, from Kawecki Berylco Industries, Incorporated; and sodium (metal lump), from J. T. Baker Chemical Company. Helium and ultrahigh purity N_2 gas were obtained from Air Products, Incorporated.

Mercury stock from previous work was again cleaned and purified according to procedures described.

The apparatus used in the evaporation experiments is shown in Figure 1. The assembly consists of a three-stage mercury diffusion pump in series with a Welch Duoseal forepump, a McLeod gauge to monitor manifold pressure and an evaporation unit. A large liquid nitrogen trap prevents back-diffusion of mercury vapors from the diffusion pump to the evaporation unit. All stopcocks used in the assembly are high vacuum stopcocks equipped with Teflon plug and Viton O-ring seals.

The evaporation unit (shown in detail in Figure 2) has three basic elements: (a) a three compartment Teflon trough for mercury; (b) a Teflon tipping platform shaft-mounted on the trough for the contaminants; and (c) a Teflon holder for the capillary tubings. The holder is supported by two stainless steel shafts mounted on small roller bearings. With a simple pulley and counterweight system attached to one of the shafts the capillaries can be tipped to any angle from 0°-135° from the vertical position with the aid of an outside magnet. The lighter counterweight is a small bar magnet, the heavier is a small brass weight. Both are encased in Teflon to minimize impact on the glass walls of the bell jar.

Dropping the contaminants into the trough is accomplished by means of a tipping arm attached to pulley. A fine steel wire holds the contaminant platform in a horizontal position and the latter is prevented from tipping over to the rear by a small strip of thin brass shim just behind the trough.

The mercury trough is screwed onto a stainless steel hinge anchored to a removable aluminum base. Behind the trough is a Teflon-clad bar magnet connected to the bottom rear of the trough by a short piece of cotton thread. With this set up it is possible to tip the mercury trough forward by means of an outside magnet, far enough to dump its content into a rectangular glass funnel placed just below the capillary holder. A glass tube chutes the dumped materials to the cold finger on the bottom half of the bell jar.

The support for the basic elements of the evaporation unit are screwed onto a three-legged aluminum base. The upper base plate was cut full of holes leaving just enough material to support the basic evaporation unit. It is also ringed with a viton-O-ring to prevent the unit from rocking while inside the bell jar.

The bell jar has a 12-cm O.D. mated joint equipped with viton-O-ring gasket. The lower half of the bell jar is connected to the vacuum manifold via a high vacuum stopcock. A second stopcock on the opposite side is used to introduce inert atmosphere to the system. The lower half of the bell jar has a cold finger (6 cm O.D. and 5.5 inches long). It rests on a rubber-padded aluminum support on top of a stainless steel dewar with the full length of the cold finger inside the dewar.

The bell jar system is enclosed in a plexiglas air bath equipped with a 60 watt bulb heater and thermoswitch for temperature control. A small thermometer with the mercury bulb as near as possible to the capillaries, is placed inside the bell jar to monitor the temperature.

All Teflon parts of the evaporating unit are baked and degassed at 250°C in a small vacuum coater before assembly.

The mercury trough is cleaned by unscrewing it from the stainless steel hinge, removing the contaminant platform and completely immersing the trough successively in the following solutions in a sonic bath: 10% nitric acid, double distilled water, and absolute alcohol. It is then dried at 60°C and the unit assembled before placing it in the vacuum chamber.

II. Experimental Procedures

A. Preparation of capillary tubing for evaporation experiments

Pyrex capillary tubing 5.5 cm long is cut from standard stock. The flatter and more clearly cut end is lapped under water in No. 400 and then in No. 600 carbonundum paper until the surface is flat and the outer edge free of cracks. The capillary is then cleaned by aspirating while immersing about half the length of the polished end of the tube for three minutes successively into the following solutions in a sonic bath, double distilled water, 10% nitric acid solution, double distilled water, acetone or absolute alcohol. The capillary is then oven dried at 110°C and the unpolished end sealed using an oxygen-natural gas flame. The capillary diameter is measured using a Unitron Microscope equipped with a micrometer controlled mechanical stage.

B. Measurement of evaporation rate

The vacuum chamber housing the evaporation unit is degassed at ambient temperature at least overnight for every run prior to placing the mercury and the contaminant in the chamber. With the mercury diffusion pump in operation and the trap immersed in liquid nitrogen, the vacuum chamber can be pumped down to 10^{-6} Torr in about an hour.

Three clean capillary tubings whose diameter have been determined are placed in the holder and adjusted to proper lengths. This is to assure that the polished ends will completely dip inside the corresponding troughs without touching the trough's edges. The object here is to have the capillary ends completely immersed in and surrounded by mercury or the amalgam solution to avoid trapping any pressurizing gas when the capillaries are being

filled. Adjustment of the relative position of the pulley counterweights maybe necessary so that the capillaries can be positioned at will from the vertical to the dipping position and back by moving a magnet up and down outside the vacuum chamber. The magnet is clamped to a lead screw vertical manipulator to effect a more uniform and positive control of the capillary holder.

With the exception of the amalgams of sodium and lithium which were prepared under atmospheric conditions before introduction to the vacuum chamber because of handling difficulties with the bare metals, the contaminants were added to and dissolved in mercury under high vacuum (less than 10^{-5} Torr).

Each contaminant is cut with a clean stainless steel blade and weighed to 0.05 milligram on a five-lace Mettler balance so as to make a 200 ppm solution when dissolved in a preweighed amount of mercury. Each trough holds about 12 gms of mercury without spillage with the capillaries in the dipped position.

In the case of sodium and lithium, the freshly cut metal is weighed to the nearest 0.05 mg in a glass vial and a small amount of mercury immediately added. The additional mercury needed to make 200 ppm amalgam solution is then exactly weighed and subsequently added just prior to placing the amalgam in the vacuum chamber.

The contaminant metals are placed on slots provided in the tipping platform before the individual troughs are filled with preweighed mercury. The upper half of the bell jar is then clamped in position and the vacuum chamber evacuated. As soon as sufficient vacuum is attained (1×10^{-5} Torr or less) the contaminants are dropped into the mercury. When the contaminants have dissolved, the open end of the capillary tubings are slowly immersed in the contaminated mercury, and helium is slowly introduced to force the contaminated mercury into the capillaries. The filled capillaries are then positioned vertically and the chamber evacuated to 10^{-5} Torr or less. The excess amalgam is then dumped into the cold finger and frozen with liquid nitrogen. This is necessary in order to maintain as low a

concentration of mercury as possible in the space above the capillaries while the manifold pressure is maintained at less than 10^{-5} Torr as measured by the McLeod gauge. Time zero is taken after the stainless steel dewar is filled with liquid nitrogen. The dewar is refilled automatically every two hours by a means of a simple timer-solenoid valve arrangement.

One of the three capillaries in every evaporation rate experiment contains just pure mercury and serves as internal control. The rate of evaporation is determined by measuring the change in length of mercury in the capillary with time using a cathetometer. Standard deviation in length measurement for five readings is $\pm.002$ cm. Thus, the maximum error in measurement is estimated to be 0.004 cm.

C. Surface tension measurements

The surface tensions of mercury and a few selected amalgams (200 ppm) were measured by maximum bubble pressure method using an apparatus patterned after Sugden[11]. Ultrahigh purity nitrogen was used as the bubbling gas. The narrow jet had an internal radius of 0.061 cm, and an external radius of 0.091 cm, the wide jet, an internal radius of 0.296 and an external radius of 0.393 cm. With the exception of the almagam of sodium, the amalgams were prepared inside the bubbling chamber by dropping freshly cut metals into preweighed amounts of mercury. In the case of sodium, an amalgam concentrate was prepared under atmospheric conditions and then added to bulk mercury in the bubbling chamber. Final calculations of surface tensions were performed in the manner described by Bosworth[12].

References

1. A. H. Ellison and S. B. Tejada, NASA CR 72441, July 23, 1968.

2. V. K. LaMer, "Retardation of Evaporation by Monolayers: Transport Processes", Academic Press, New York, 1966.

3. G. L. Gaines, Jr., "Insoluble Monolayers at Liquid-Gas Interfaces", Interscience Publishers, New York, 1966.

4. W. Lee, I and EC Product Research and Development, $\underline{7}$, 66 (1968).

5. International Critical Tables.

6. O. A. Timofeevicheva and P. P. Pugachevich, Doklady Akad. Nauk, U.S.S.R., $\underline{134}$, 1093 (1959); C.A. $\underline{55}$, 8235C.

7. C. Kemball, Trans. Faraday Soc., $\underline{42}$, 526 (1946).

8. W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions", Prentice-Hall, Inc., New York, 1938.

9. Chemical Rubber Company, Handbook of Physics and Chemistry, 36th ed., (1954-1955).

10. S. N. Zadumkin and V. G. Egiev, Fiz. Metal. i Metalloved, $\underline{22}$, 121 (1966); C.A. $\underline{65}$, 17839h.

11. S. Sugden, "The Parachor and Valency", George Routledge and Sons, Ltd., London, 1930.

12. R. C. L. Bosworth, Trans. Faraday Soc., $\underline{34}$, 1501 (1938).